

# Research of The Reduction of Oxidized Copper and Iron Compounds with Local Reducing Agents

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**Abstract:** The article examines the thermodynamic possibilities of the process of obtaining a pure metal by treating oxidized copper compounds with a liquid organic substance. The object of the study was copper (II) oxide and ethyl alcohol, on which the physicochemical changes occurring in the redox reactions between them were analyzed. The laws of the relationship between temperature and Gibbs energy and the equilibrium constants of a chemical reaction in a reaction system are defined and described in the form of various graphs in order to more clearly explain the essence of the process. The optimal conditions for the normal course of the process have been determined. Recommendations are given for the use of nanoparticles containing pure copper powder obtained as a result of the reaction.

**Keywords—** metallurgy, magnetite, copper, reduction, ethyl alcohol, factors, pyrometallurgy.

## 1. INTRODUCTION

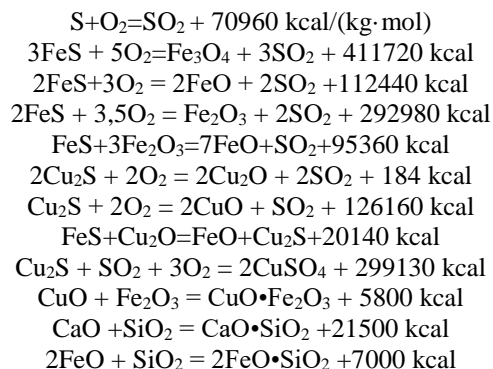
In some countries, copper ores in the form of oxides or mixtures (i.e., oxides and sulfides) are found, so the technology of copper extraction in them is based on a combined method [1-2]. For example, ore or concentrate is first burned by oxidation and then separated by hydrometallurgical methods. Alternatively, crude copper can be obtained by reducing the oxidized copper concentrate formed after firing in the presence of coke in the Shaft and Reverberatory furnaces. This technology is preferred in that it is less phased than its predecessors. Therefore, it is important to know the technological parameters of the oxidation process of sulfide minerals [3-8].

The object of research is chalcopyrite copper concentrates of Almalyk Mining and Metallurgical Combine (AMMC), the chemical composition of which is as follows: Cu - 20%, S - 36%, Fe - 33%, SiO<sub>2</sub> - 6%, CaO - 0.5%, etc.

The results of the phase analysis showed that AMMC concentrates contained chalcopyrite (CuFeS<sub>2</sub>), covellin (CuS), pyrite (FeS<sub>2</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>), quartz (SiO<sub>2</sub>) and salts of alkali and alkaline-earth metals. In these concentrates, the distribution of copper metal to chalcopyrite and covellin minerals was approximately 9:1.

The process of roasting copper concentrates is carried out in the "Hot layer" furnace. At the same time, the volume of oxygen in the air sprayed into the furnace for normal operation of the process is 21% and the degree of desulfurization is 96.47%. The temperature is adjusted to 850 °C for complete firing. The pressure of the air supplied from the bottom of the furnace is 12 MPa [9-13]. When the concentrate is loaded into the furnace, several physicochemical processes take place under the influence of temperature and oxygen. Initially, sulfide minerals decompose under the influence of temperature. The resulting

low-sulfide minerals and sulfur vapor are then oxidized by oxygen. The thermochemical reactions of the process are as follows:



An increase in the concentration of oxygen in the sprayed air is one of the factors leading to the complete and perfect oxidation of sulfur. The essence of this process is the tendency of copper and its additives to oxygen. Because this tendency is of great importance for high-temperature compounds that melt [14-17]. This depends on the Gibbs energy content or the degree of dissociation of the oxides in the solution, that is, the pressure of the gases formed as a result of the dissociation at that temperature, and this pressure changes with temperature. The chemical composition of the oxidized copper concentrate obtained is presented in Table 1.

**Table 1:** Chemical composition of oxidized copper concentrates according to the study, %

Cu	Fe	S	O
25.15	41.49	1.27	19.62
SiO <sub>2</sub>	CaO	Others	Total
7.55	0.63	4.29	100

Comparing the results of the initial enrichment and Table 2, it can be seen that the concentration of copper increased by 5.15% after oxidative annealing. This oxidized copper concentrate is magnetically separated to remove up to 30% of the iron content. When the resulting oxide copper concentrate is mixed with a sulfide concentrate containing 16-18% copper, it is possible to obtain a mixed copper concentrate of 25-26%. When a mixture of copper oxides and sulfides is melted in a Reverberatory furnace, copper compounds in the form of oxides oxidize the iron sulfides in the matte to the slag phase, resulting in a 30% increase in the concentration of copper in the matte [18-25].

## 2. MATERIALS AND METHODS

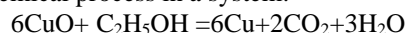
In metallurgy, coke, coal, pistachio coal, lignite, and similar hard materials are commonly used as reducing agents. However, the use of carbon-containing liquid reducing agents is not often observed. This is because carbon-containing liquid reducing agents are used as fuel. For example, fuel oil is used as a heat source for heating metallurgical furnaces. This is because the ignition temperature of fuel oil is lower than that of solid fuels, which means that it ignites quickly. Due to the high consumption of fuel oil in metallurgy, the demand for fuel oil is very high. This requires research into the use of other liquid reducing agents in metallurgical processes other than fuel oil. One such regenerator is organic alcohols, the most common of which, ethyl alcohol, was selected as the object of study [26-32].

Ethyl alcohol (wine alcohol, ethanol) formula  $C_2H_5OH$  is an important representative of monohydric aliphatic alcohols. Molar mass 46.069 g/mol. It is a colorless, pungent, alcoholic liquid. Liquidus temperature  $-114.5^\circ C$ , boiling point  $78.39^\circ C$ , density  $789.27 \text{ kg/m}^3$  (at  $20^\circ C$ ). It mixes indefinitely with water to form an azeotropic compound containing 95.57% alcohol and 4.43% water. There are 2 methods used to obtain absolutely pure alcohol. In Method 1, a small amount of benzene is added to the aqueous alcohol and the resulting mixture is fractionated. In this case, first a mixture of water, alcohol and benzene, then a mixture of alcohol with benzene, and finally, pure alcohol is expelled. In Method 2, 96% alcohol is heated with calcium oxide or heated copper (II) sulphate. The bulk of the water is removed, and 0.2-0.3% of the water retained in the alcohol is separated by the addition of metallic calcium or magnesium to the alcohol [33-41].

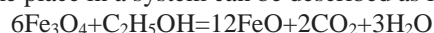
Magnetite (magnetic iron ore) is a mineral belonging to a small class of complex oxides. Chemical composition -  $Fe_3O_4$ . The composition and properties are variable, depending on the conditions of formation. The cube crystallizes in syngonium to form octahedral crystals and rhombododecahedral solid granular aggregates. The color is brownish-black, shiny like metal. Hardness 5.5-6.0; density  $5200 \text{ kg/m}^3$ . It has strong magnetic properties. Titanium (IV) oxide ( $TiO_2$ ) is called titanium magnetite and chromium (II) oxide is called chroma magnetite. Occurs in igneous rocks, hydrothermal deposits, and sometimes sedimentary rocks. Magnetite is the main raw material from which iron is extracted. The largest deposits of magnetite are in Russia

(Kursk magnetic anomaly), Ukraine (Krivoy Rog, Kremenchug iron ore deposits), Sweden, the United States and other countries [42-48].

Knowing the reducing properties of ethyl alcohol, the process of reducing copper from oxidized copper compounds was determined by several experiments. The reaction of a chemical process in a system:



Chalcopyrite also absorbs rare metals and precious semi-finished products of mineral formation due to the formation of magnetite when oxidized. the process of return with spirit was studied. Accordingly, the basic chemical reactions that take place in a system can be described as follows:



## 3. RESULTS AND DISCUSSION

### 3.1. STUDY OF THE THERMODYNAMICS OF THE REDUCTION OF COPPER OXIDE WITH ETHYL ALCOHOL

In the study, dry copper (II) oxide was first ground in a mortar and 70% ethyl alcohol was poured over it. In this case, the components were obtained in such a mass ratio that the resulting liquid: density ratio was 1: 1 [49-52]. The resulting mixture was heated in a laboratory muffle furnace to a temperature of  $627^\circ C$ . Qualitative, quantitative and thermodynamic analysis of the powder formed as a result of the reaction was carried out. The process was carried out in an oxygen-free environment.

The thermodynamic values of the starting materials are given in Table 2.

**Table 2:** Appropriate thermodynamic quantities of substances (298 K)

Substances	CuO	$C_2H_5OH$	Cu	$CO_2$	$H_2O$
$\Delta H$ (kJ/mol)	-157.03	-234.8	0	-393.38	-228.597
$\Delta G$ (kJ/mol)	-127.6	-167.96	0	-394.38	-242.827
$\Delta S$ (kJ/mol)	42.63	281.38	31.05	218.68	188.724

Using the thermodynamic values of these substances, we determine the probability that a chemical process will take place at several temperatures. First, let's look at the results of a chemical process under standard conditions:

$$\Delta H_{reaction}^{298} = -295.572 \text{ kJ}$$

$$\Delta G_{reaction}^{298} = -583.681 \text{ kJ}$$

$$\Delta S_{reaction}^{298} = 0.653 \text{ kJ}$$

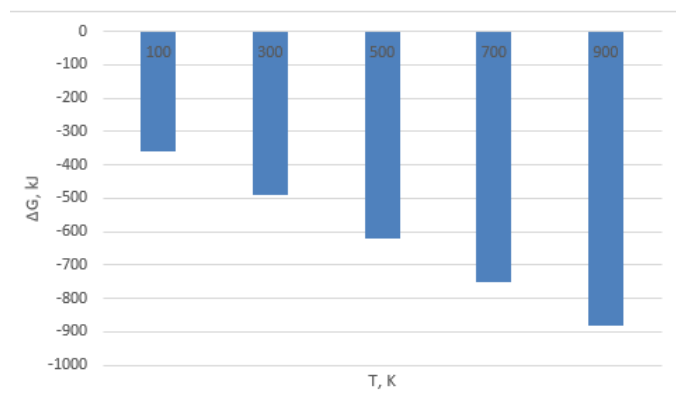
From the results under standard conditions, it can be seen that the enthalpy value of the reaction is negative (exothermic), i.e., heat is released as a result of the reaction. The value of the free energy of the reaction is also negative, which means that the chemical reaction can flow independently under the given conditions. In order for the

process to proceed under standard conditions, the activation energy of the starting materials must be given. Table 3 shows how the increase in temperature after the onset of a chemical reaction in the system affects the reaction rate [53-54]:

**Table 3:** 100 – 900 K the values of the change in Gibbs energy of the reaction in the temperature range

N <sub>o</sub>	ΔH, kJ	R	ΔS kJ	T, K	ΔG, kJ
1	-295,572	8,31	0,653	100	-360,872
2	-295,572	8,31	0,653	300	-491,472
3	-295,572	8,31	0,653	500	-622,072
4	-295,572	8,31	0,653	700	-752,672
5	-295,572	8,31	0,653	900	-883,272

In Table 3, the Gibbs energy value of a chemical reaction decreases as the temperature increases by every 200 units. It was found that the probability of a reduction reaction of copper (II) oxide with ethyl alcohol increases with increasing temperature. This will allow us to put this process into practice.



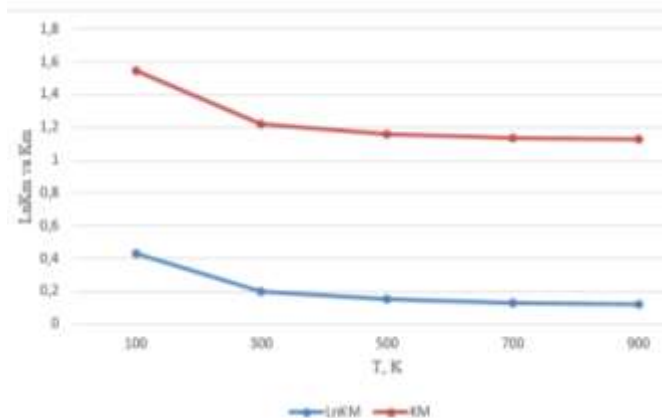
**Fig.1.** Temperature dependence of the change in Gibbs energy value during the reduction of copper (II) oxide with ethyl alcohol

Figure 1 shows the change in the Gibbs energy values of the reaction system as the temperature rises during the production of copper powder by the reduction of copper (II) oxide with ethyl alcohol. From this, it can be seen that the Gibbs energy of the reaction decreases linearly with each increase in temperature by 200 units.

From the values of the Gibbs energy of the reaction in the system, the values of the equilibrium constant are found and are shown in Table 4:

**Table 4:** 100 – 900 K values of change of chemical reaction equilibrium in the temperature range

N <sub>o</sub>	T	LnK <sub>M</sub>	K <sub>M</sub>
1	100	0,434262	1,543824
2	300	0,197141	1,217916
3	500	0,149716	1,161505
4	700	0,129392	1,138136
5	900	0,1181	1,125357



**Fig.2.** Temperature dependence of the change in the value of the equilibrium constant during the reduction of copper (II) oxide with ethyl alcohol

From the graph shown in Figure 2, it can be seen that the chemical equilibrium constant decreases sharply as the temperature increases from 100 degrees to 300 degrees. The chemical equilibrium constant is stabilized in the temperature range from 300 to 900 °C. The values in Table 3 show that the equilibrium constant decreases with increasing temperature. This is explained by the fact that the enthalpy value of the reaction is negative. This is because an increase in temperature in exothermic reactions leads to a decrease in the correct reaction rate.

### 3.2. STUDY OF THE THERMODYNAMICS OF THE PROCESS OF REDUCTION OF MAGNETITE WITH ETHYL ALCOHOL

The thermodynamic values of the starting materials are given in Table 5.

**Table 5:** Appropriate thermodynamic quantities of substances (298 K)

Substance s	Fe <sub>3</sub> O <sub>4</sub>	C <sub>2</sub> H <sub>5</sub> O H	FeO	CO <sub>2</sub>	H <sub>2</sub> O
ΔH(kJ/mol)	-822.2	-234.8	-272	393.38	228.597
ΔG(kJ/mol)	740.32	-167.96	251.46	394.38	242.827

$\Delta S(\text{kJ/mol})$	87.4	281.38	60.75	218.6 3	188.72 4
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Using the thermodynamic values of the starting materials, we determine the probability that a chemical reaction will take place at several temperatures. Let's take a look at how the system works under standard conditions:

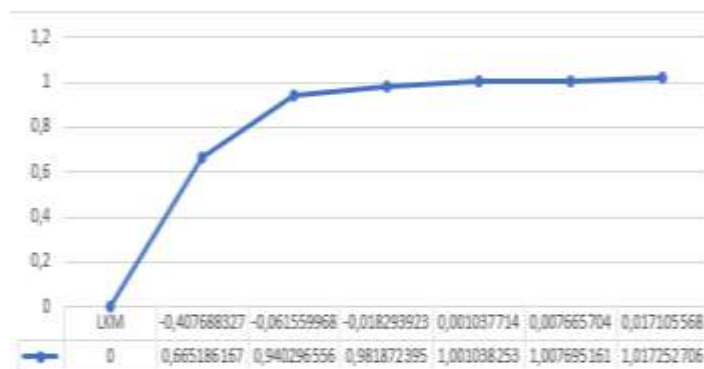
$$\begin{aligned} \Delta H_{\text{Reaction}}^{298} &= 431.449 \text{ kJ} \\ \Delta G_{\text{Reaction}}^{298} &= 75.119 \text{ kJ} \\ \Delta S_{\text{Reaction}}^{298} &= 0.9266 \text{ kJ} \end{aligned}$$

This means that under standard conditions, a chemical process takes place in the system. However, the activation energy of the starting materials is required for the chemical process to take place. Table 6 shows how the increase in temperature after the onset of a chemical reaction affects the reaction rate:

**Table 6:** Appropriate thermodynamic quantities of substances (298 K)

H	R	S	T	G
431,449	8,31	0,9266	100	338,789
431,449	8,31	0,9266	300	153,469
431,449	8,31	0,9266	400	60,809
431,449	8,31	0,9266	470	-4,053
431,449	8,31	0,9266	500	-31,851
431,449	8,31	0,9266	550	-78,181

From the Gibbs energy values of the reaction, the values of the equilibrium constant are determined and plotted (Fig.3):



**Fig.3.** Temperature dependence of the change in the value of the equilibrium constant during the reduction of magnetite oxide with ethyl alcohol

#### 4. CONCLUSION

When studying the thermodynamic possibilities of the process of reduction of oxidized copper compounds with ethyl alcohol, it was found that at a temperature of 627°C (900 K) the equilibrium in the chemical reaction shifts to the right, i.e., to the recovery of the metal. During the process, due to the formation of gas and water, the product was found to be environmentally friendly, while preventing contamination with harmful (unnecessary) elements. The obtained copper powder is liquefied in smelting furnaces to obtain metal ingots.

When studying the thermodynamic possibilities of the process of reduction of magnetite with ethyl alcohol, it was found that at a temperature of 197 °C (470 K) the equilibrium shifts to the right in the chemical reaction, ie to the product formation side. The system does not emit any environmentally toxic gases and dust during the chemical reaction and at the end of the process.

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